

# Mechanistic Investigation for the Rechargeable Lithium-Sulfur Batteries

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**Project ID: ES285**

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# Overview

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## Timeline

- **Start: 10/01/2015**
- **Finish: 09/30/2017**
- **Percentage Complete: 70%**

## Budget

- **Funding received in FY16: DOE: \$300k**
- **Funding for FY2017: DOE: \$300K**

## Barriers addressed

- To enable high energy Li-S battery (A,B,C,D,E)
- Li-S batteries with long calendar and cycle life (C,E)
- Practical high performance cathode material synthesis (A,C,D,E)

## Collaborators

- Johnson Controls Inc.
- University of Washington Seattle.
- University of Arkansas.
- Pacific Northwest National Laboratory (PNNL).
- Department of Chemistry, Wuhan University
- Department of Chemistry, Wuhan University of Science and Technology
- Beijing Institute of Technology.
- Institute of Physics, Chinese Academy of Sciences

# Relevance and Project Objectives

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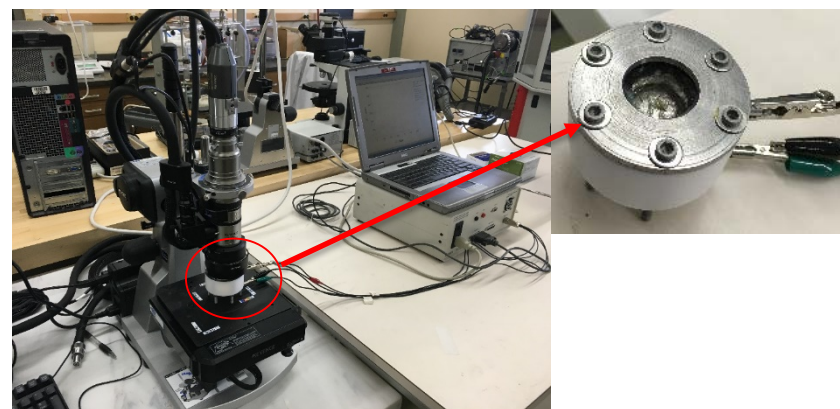
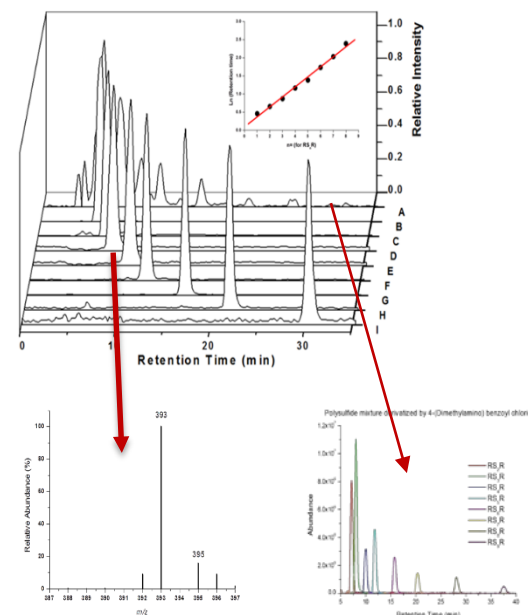
- **Overall Objectives**
  - ✓ *Fully understand the detail mechanism of the sulfur redox reaction.*
  - ✓ *Exploration of the engineering solutions for the development of long cycle life, high capacity Li-S batteries.*
- **Objectives this period: to enable high energy, high cycle life Li-S batteries through fundamental investigation.**
  - ✓ *Development of an in-situ 3D microscopic and electrochemical techniques (including electrochemical cells) to study the surface conditions of the electrodes in a Li-S batteries during the charge and discharge.*
  - ✓ *By means of the unique in-situ HPLC-Electrochemical method we developed in FY16, to understand the complex mechanism of sulfur cathode redox reaction in Li-S batteries (to guide the sulfur cathode material, electrolyte synthesis and cell engineering).*
  - ✓ *Continue the investigation of “shuttle effect” by studying the chemical equilibrium of the dissolved elemental sulfur and polysulfide ions, which including the search of the adequate electrolytes for long cycle life Li-S batteries and the additives for stable SEI formation on the Li anode.*

# Milestones

Month/Year	Milestones	Status
Dec/16	Complete the design and validation of the <i>in-situ</i> electrochemical – microscopic cell for the <i>in-situ</i> investigation of Li anode during cycling.	Completed
Mar/17	Complete the study of interaction between the dissolved elemental sulfur and polysulfide ions with both the electrolytes and Li anode.	Completed
Jun/17	Complete the investigation of the chemical equilibriums among dissolved polysulfide ions during the courses of discharge and recharge of Li-S batteries.	On schedule
Sep/17	Complete the preliminary engineering design and test for the rechargeable Li-S battery including electrode design and cell design.	On Schedule

# Approaches

- A combination of **High Performance Liquid Chromatography (HPLC)/Mass Spectroscopy (MS)** together with *in situ* electrochemical measurement in a specially designed cell. The electrochemically formed dissolved polysulfide ions can be separated (by HPLC) and determined (by MS).
- **Ex-situ X-ray diffraction (XRD)** and **X-ray photoelectron spectroscopy (XPS)** to investigate the surface of sulfur cathode and Li anode to elucidate the surface changes during the Li-S battery operation'
- **In-situ Keyence 3D microscope** and **electrochemical measurement** in a specially designed cell to investigate the surface modification of Li with e.g. various additives and at different stage of charge/discharge.
- Extended collaboration with other US and international academic institutions and US industrial partners.

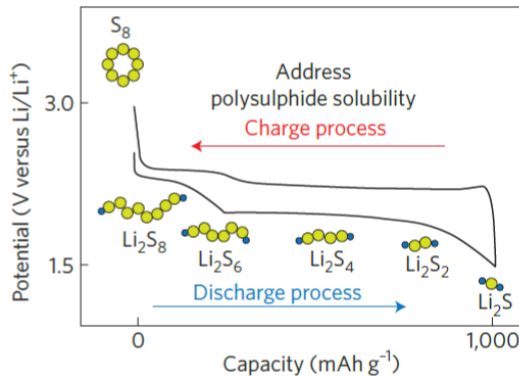


# Technical Accomplishments and Progress

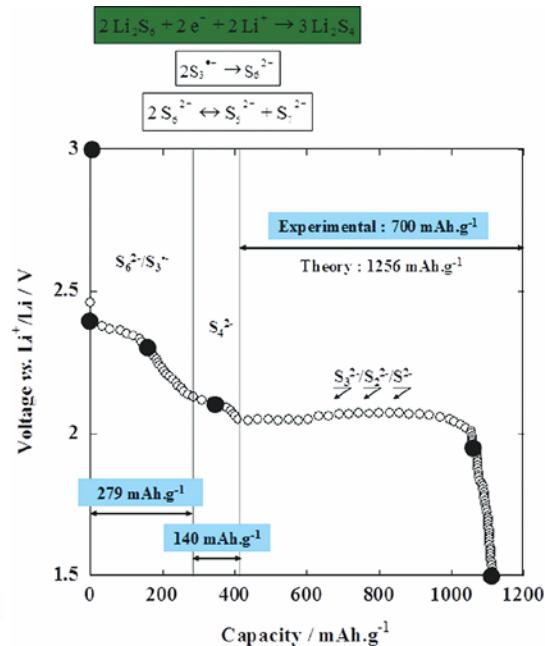
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- The in-situ HPLC/MS-Electrochemical technique was optimized. The effectiveness of the electrochemical cells were tested. The change of dissolved sulfur and polysulfide ions was determined real-time during the charge and discharge of Li-S batteries, qualitatively and quantitatively.
- Based on the real-time determination of polysulfide ions in the electrolyte, a redox mechanism was proposed which can explain the two-step discharge profile and one-step charging profile of a Li-S batteries.
- The stability of salts was studied. ALL salts were found unstable with Li in the sulfur containing DME electrolyte.
  - SEI layer was found not strong enough to prevent the attack of sulfur or polysulfide ions.
  - Some salts react with polysulfide ions.
  - $\text{LiNO}_3$  helps but cannot sustain for long period of time.
- An in-situ microscopic-electrochemical cell was designed and built. The surface of an anode was investigated real-time during the charge and discharge in the polysulfide containing electrolytes.

# Literature Review: Dissolved Polysulfides Play Important Roles

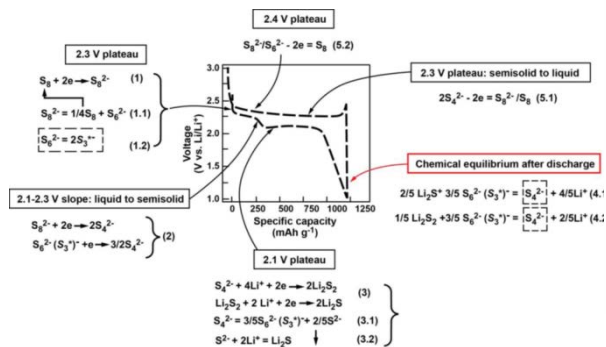


P. Bruce etc. Nat. Mater. 11(2012)19



Questions:

1. Multistep multielectron electrochemical process, why are there only two steps in the discharge curve?
2. How to quantitatively and qualitatively measure polysulfide species?



J.Xiao etc. JEC 162(2015)A474

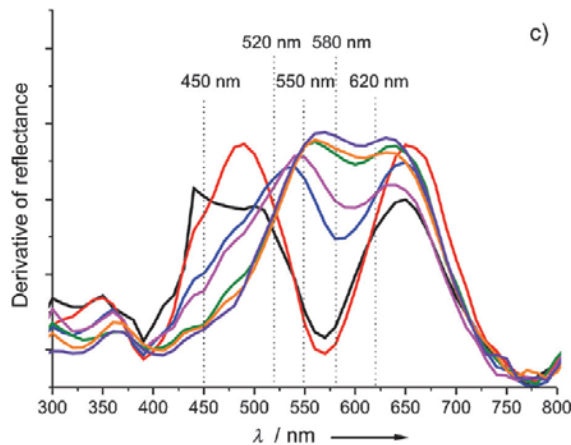
C. Barchase Anal. Chem. 84 2012 3973



## Literature Review:

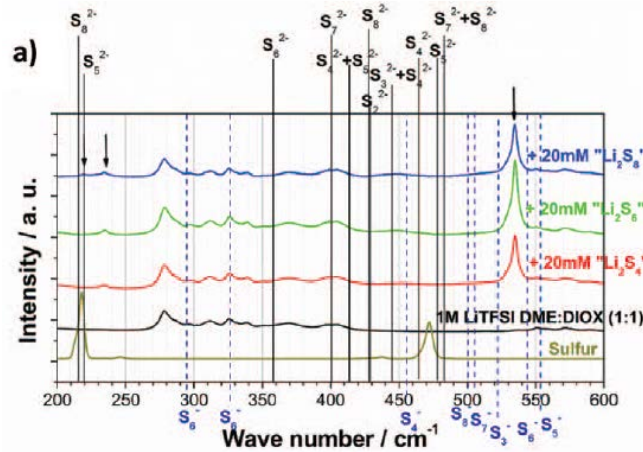
## Quantitative and Qualitative Determination of Polysulfide Becomes Critical

## UV-Vis.



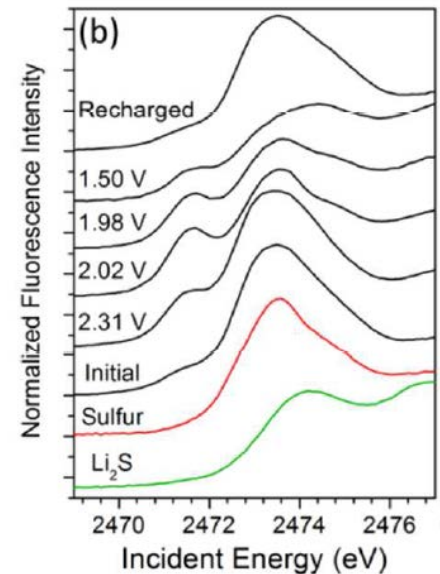
R. Dominko etc. ChemSusChem 7(2014)2167

# Raman



M Hagen etc. J. Electrochem. Soc. 160(2013)A1205

## X-Ray Absorption Near Edge



H.D. Abruna etc. RSC Adv. 4(2014)18347

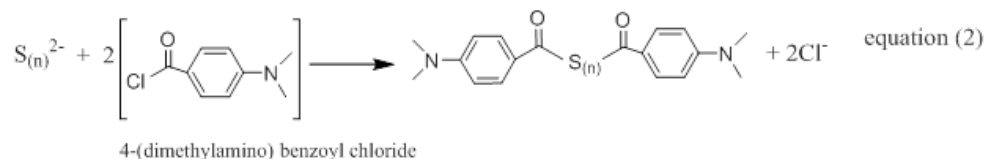
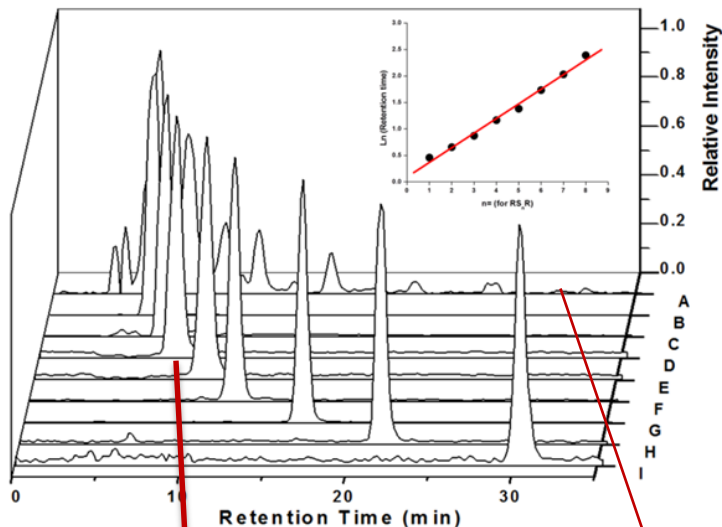
**A accurate and precise determination of polysulfides cannot be done by the above analytical techniques, they can provide estimation at the best.**

**Because it is impossible to make pure polysulfide ion with precise chain length in solution due to the chemical equilibrium and disproportionation.**

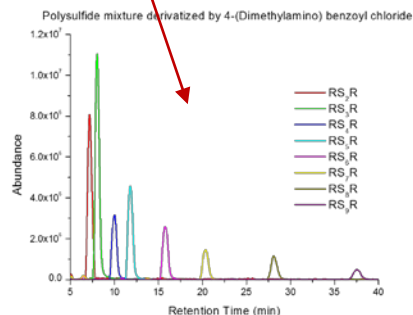
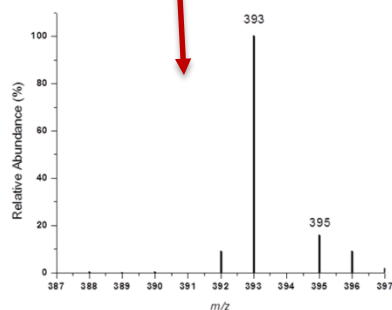
Background Slide used in FY16 review



# Polysulfides can be separated and analysis by HPLC-/UV/MS with proper complexation essay



ALL 8 polysulfides are separated and qualitatively analyzed for the first



$\text{Na}_2\text{S}$  and  $\text{S}_8$  in acetonitrile, molar ratio of  $\text{Na}_2\text{S}:\text{S}$  is 1:3

# Sulfur reacts with metallic Li and SEI is NOT stable enough to prevent the reaction

LiTFS LiTFSi LiDFOB LiBOB LiBF<sub>4</sub> LiPF<sub>6</sub> LiClO<sub>4</sub> LiTFSi/DOL

In DME solvent

SEI was effective



With Sulfur without Li

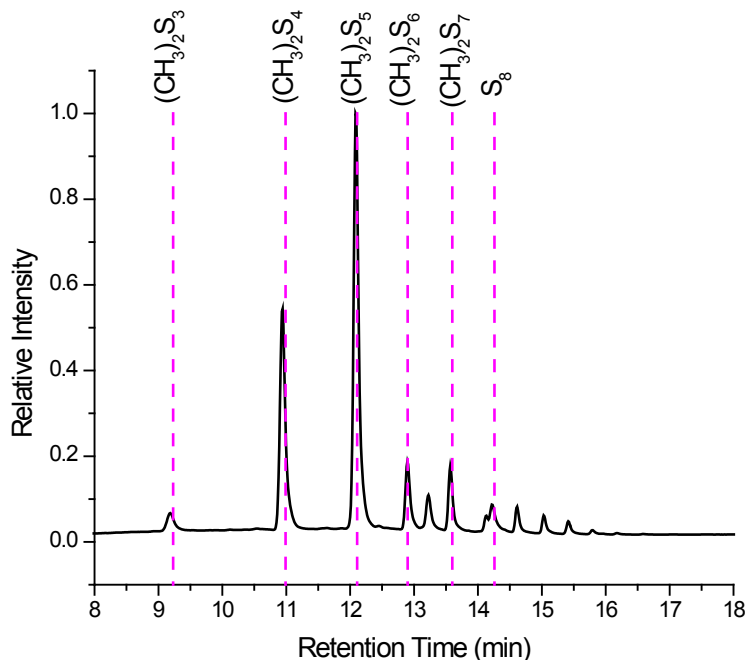
With Sulfur and Li, 1 day

With Sulfur and Li, 2 days

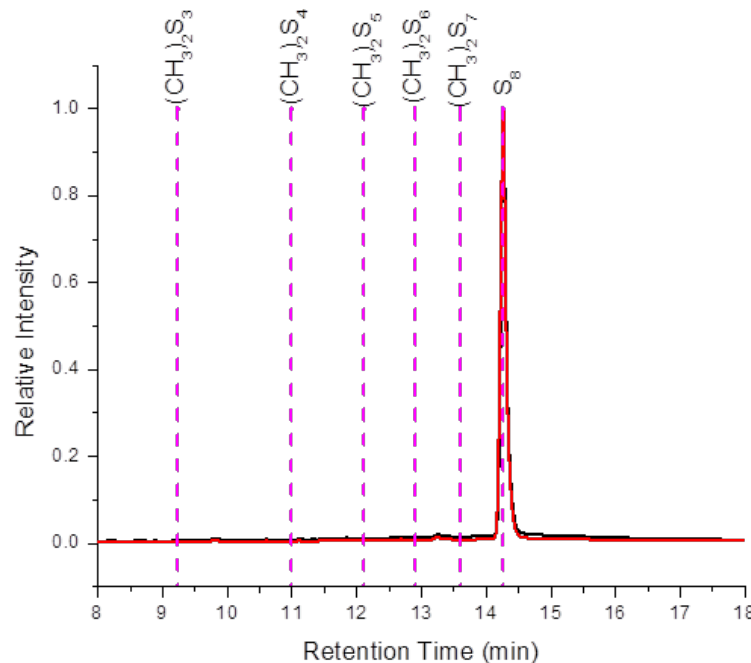
With Sulfur and Li, 4 days

With Sulfur and Li, 8 days

# Sulfur Reaction with Li



The chromatogram of LiTFSi/DME/DOL electrolyte with Li metal for 8 days then derivatized by methyl triflate.

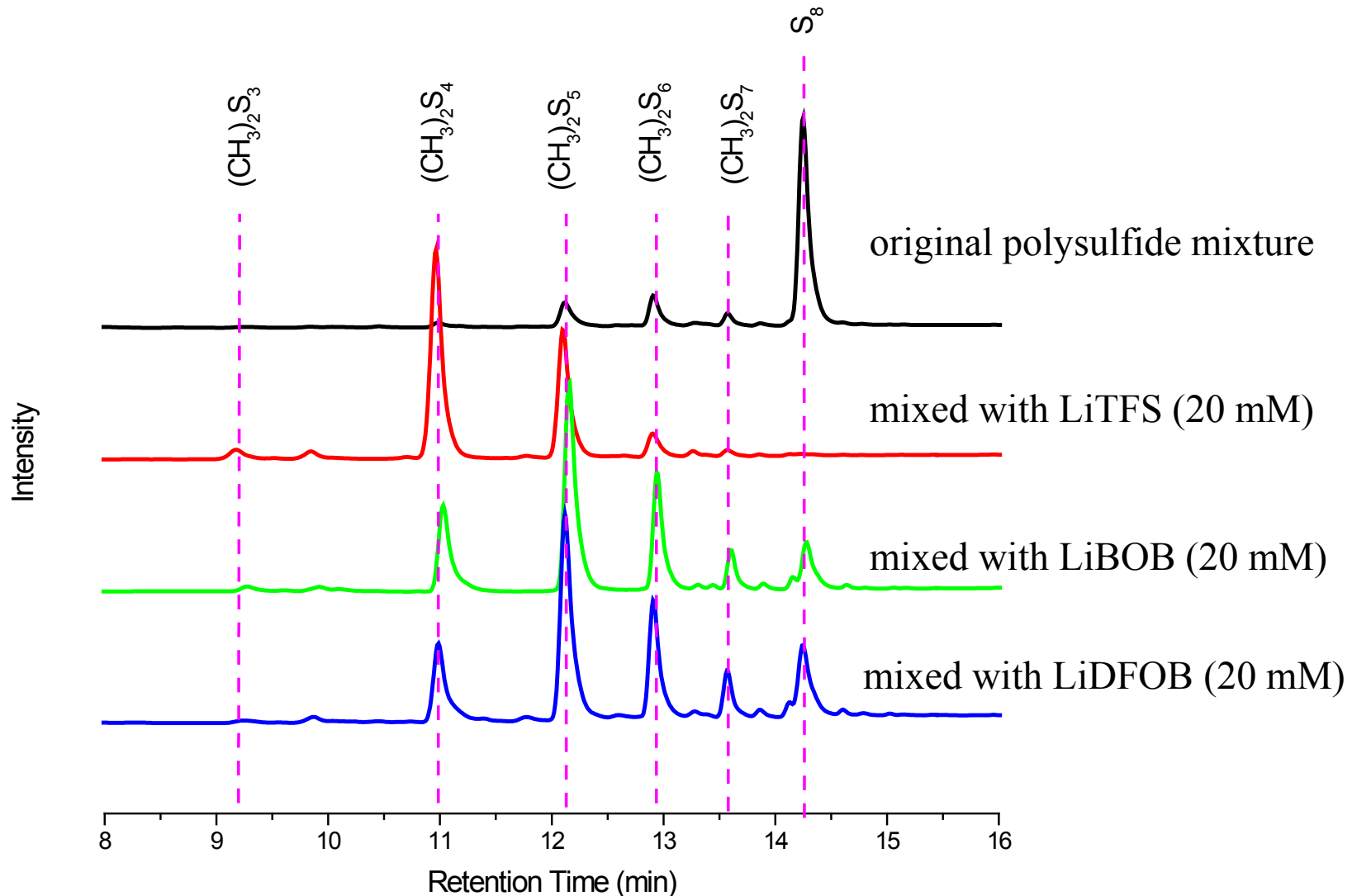


The chromatograms of LiBOB/DME electrolyte with Li metal (in black) and LiDFOB/DME electrolyte with Li metal (in red) for 8 days then derivatized by methyl triflate.

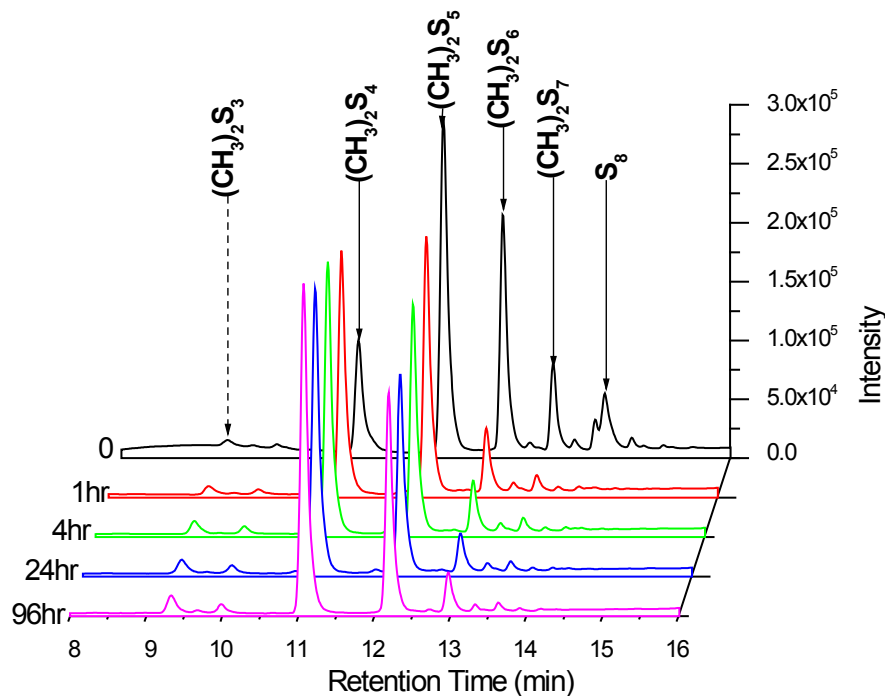
Two examples of the electrolytes with different salts:

- LiTFSi/DME/DOL cannot form effective SEI layer on Li to prevent the reaction between elemental sulfur and Li. All the sulfur became polysulfide ions after 8 days (left figure).
- The interaction between Li and elemental sulfur can be prevented in LiBOB/DME electrolyte. After 8 days, sulfur remained (right figure)

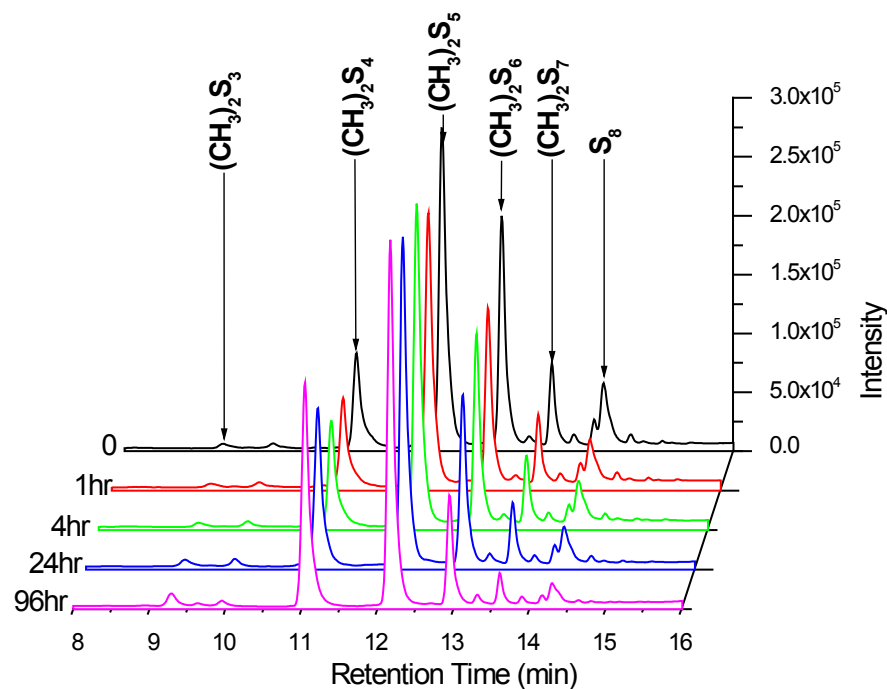
Although forming adequate SEI layer to prevent the interaction between Li and sulfur, LiDFOB and LiBOB react with Polysulfides



# **LiNO<sub>3</sub> additives cannot form a stable enough SEI layer for long term storage of Li-S batteries**

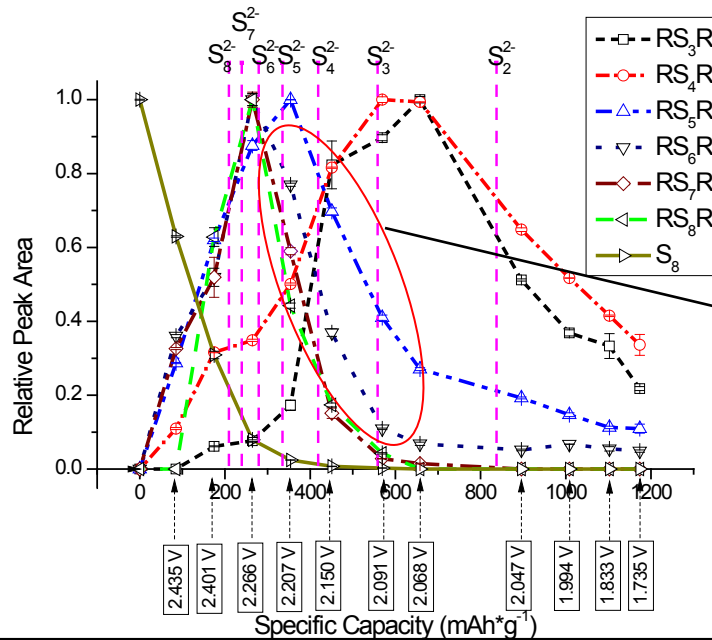


Without addition of LiNO<sub>3</sub>



With addition of 0.1 M LiNO<sub>3</sub>

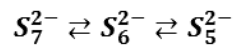
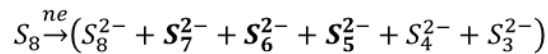
# Discharge of a sulfur cathode



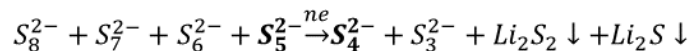
Parallel lines represent the species in equilibrium, because the ratio of concentration remains constant.

Two major chemical equilibria - two discharge plateaus.

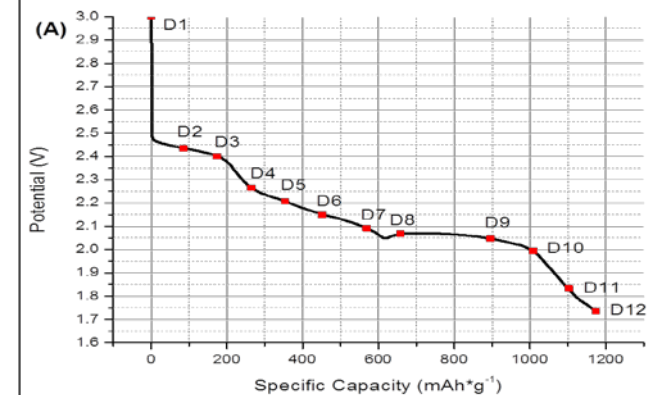
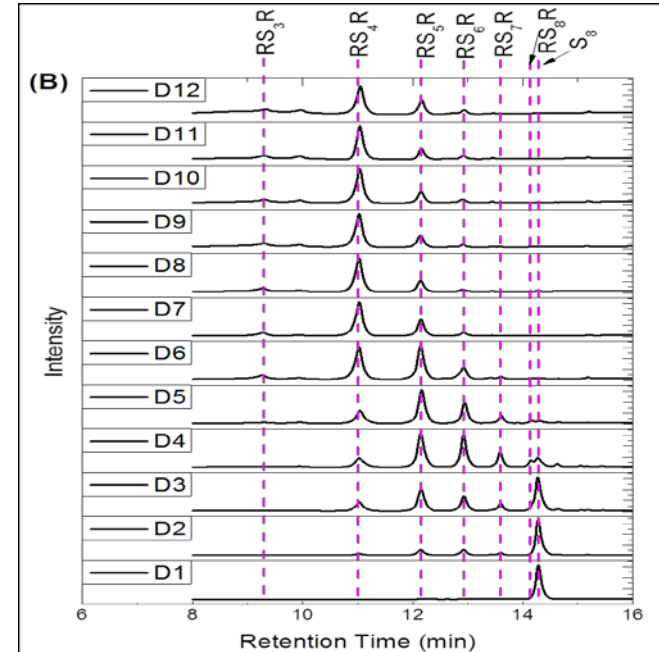
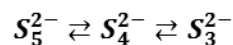
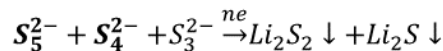
>2.3 V, first plateau, major species are bold



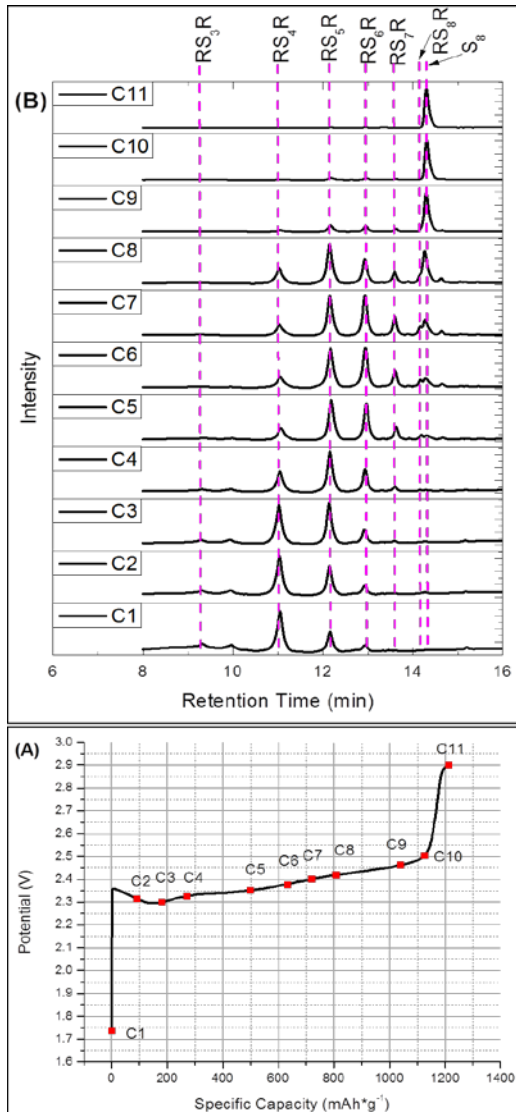
Between 2.3 and 2.1 V, major species are bold



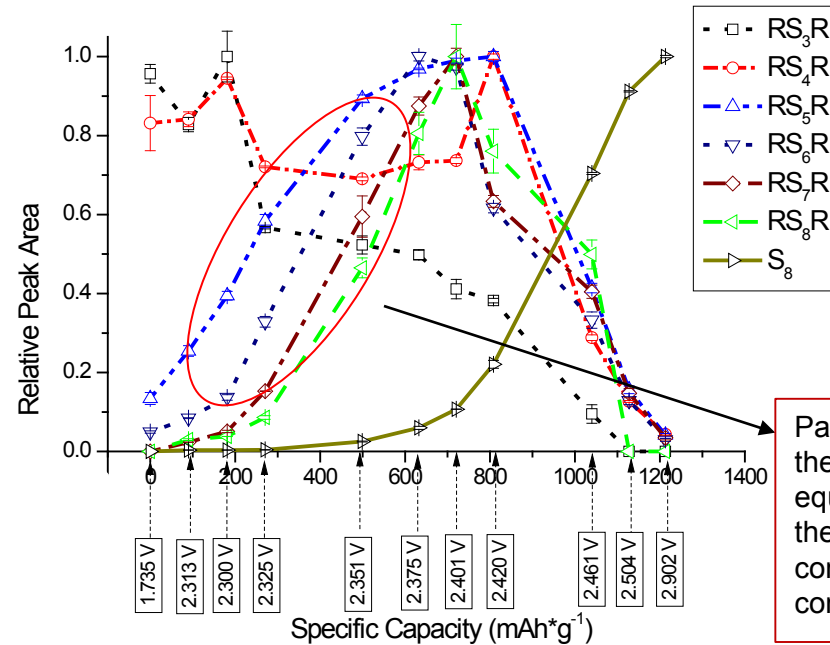
<2.1 plateau, major species are bold



# Recharge process

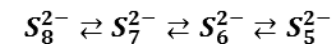
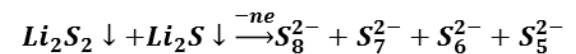


1. An single chemical equilibrium in the recharge.
2. Sulfur redox reaction is "reversible".

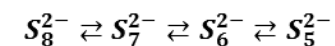
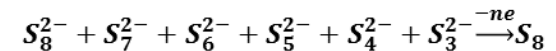


Parallel lines represent the species in equilibrium, because the ratio of concentration remains constant.

Cathode potential < 2.4 V

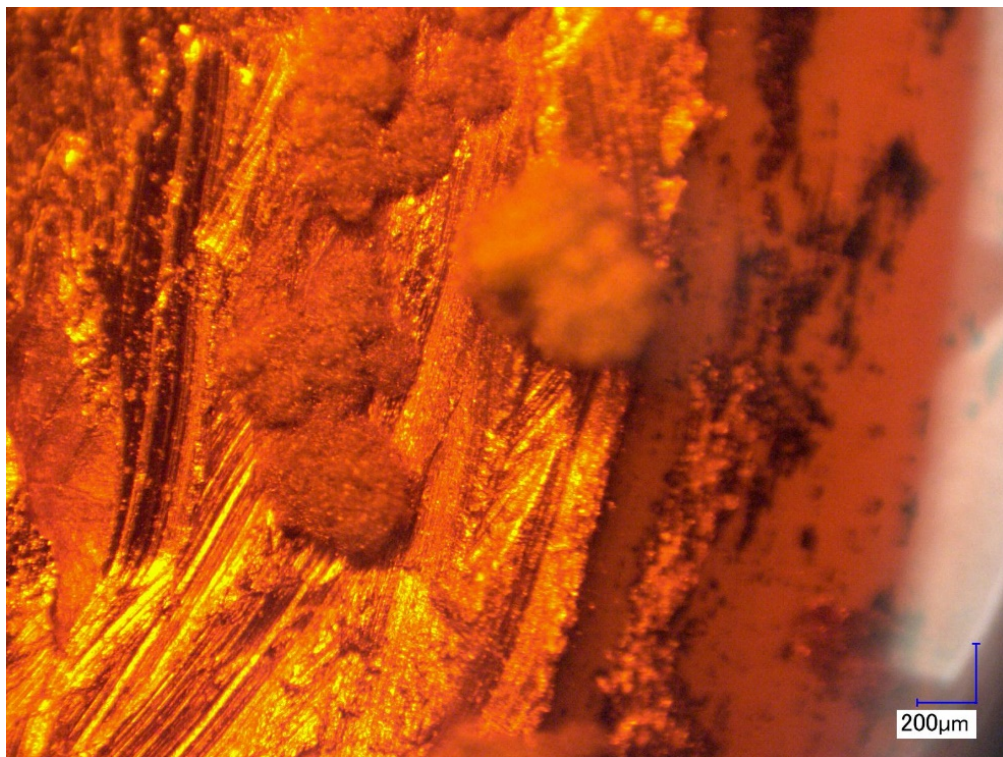


Cathode potential > 2.4 V



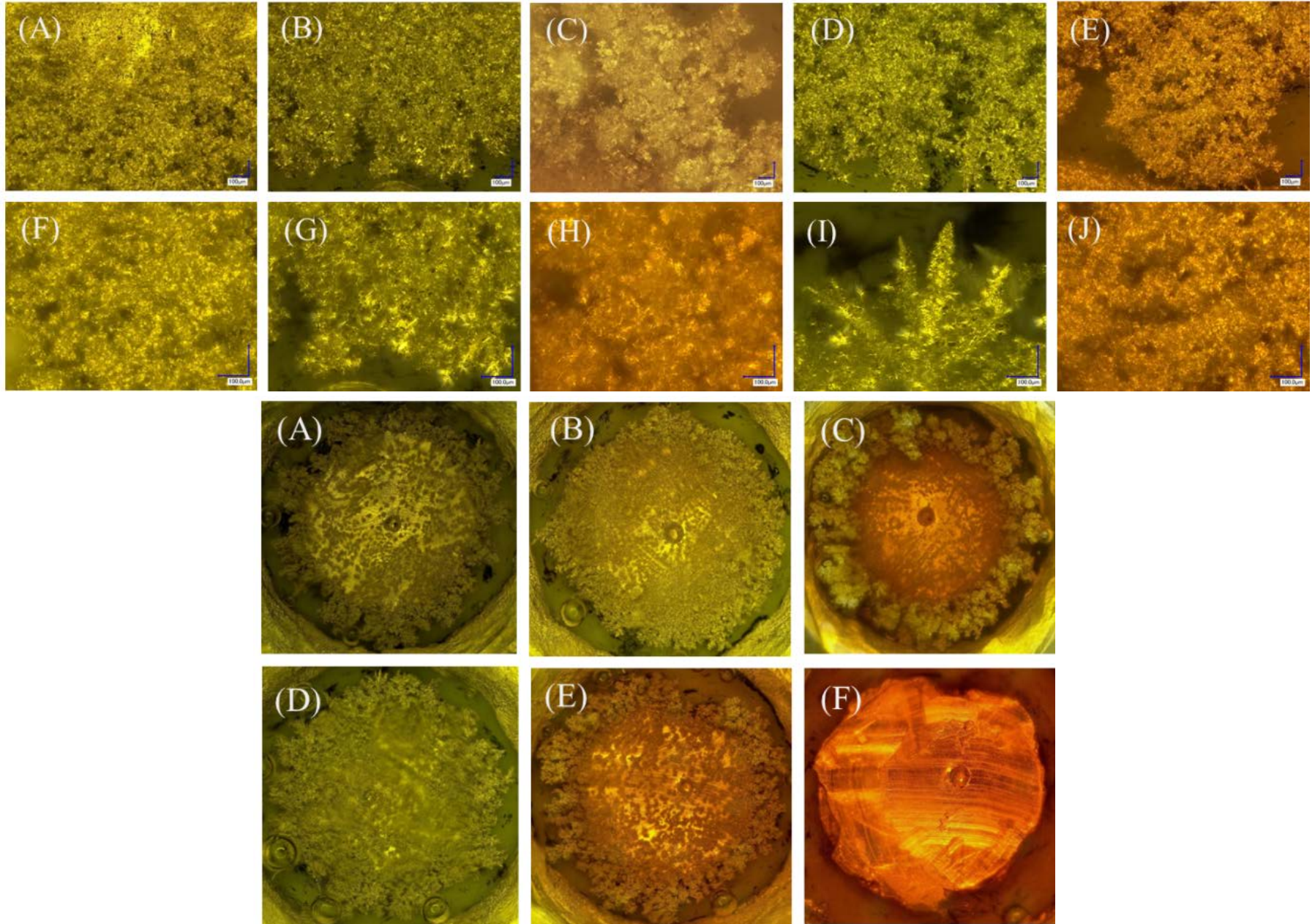


# In-situ Optical Electrochemical cell for Li Surface investigation





# Example of Li anode during operation



# Response to last year reviewer's comments

The PI and associates gratefully appreciate the positive and encouraging comments from the four reviewers.

The following are the two issues needed to be addressed by the PI.

Reviewer comments from FY16	Response
<p>This reviewer indicated that it is definitely interesting to try and understand the specific polysulfides formed during S lithiation. Although this is a worthwhile study, it is not immediately clear to the reviewer how this will lead to solutions to the polysulfide anode reaction issues or the need for so much excess electrolyte.</p>	<p>The PI respectively response that the first step leading to the solutions to the polysulfide anode reaction issues is to accurate determination of the kinds of polysulfide at various stage of Li-S battery discharge and recharge. The PI reported for the first time the most reliable (may the only) method for the in-situ determination of dissolved polysulfide ions.</p> <p>The analysis of the polysulfide trapped in the pores of a porous electrode (no excess electrolyte) is the same as in the excess electrolyte. When the polysulfide ions become derivatized, they will not further react or disproportionate.</p>
<p>This reviewer expressed confusion, and specified that there is a large amount of future work listed, which is odd because the project is scheduled to end September 2016. The reviewer believed the project concluded that polysulfide concentrations can only be measured during the first electron transfer due to subsequent reactions in the electrolyte that form multiple polysulfide species. This issue has been known in the literature for some time, explained the reviewer.</p>	<p>It was the typo from the PI, the project ends in 09/2017 instead of 09/2016.</p> <p>The PI may not explained the results well, but the method can measure any polysulfide ions in the electrolyte. What we tried to report was that we determined that the polysulfide ion formed during the first electron transfer <u>was not</u> <math>S_6^{2-}</math>, <math>S_6^{2-}</math> was reported in the literature as the initial dissolved polysulfide specie which subsequently disproportionate to other polysulfide ions as the reviewer pointed out.</p>

# Collaborations with other institutions and companies

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- **Johnson Controls Inc.**  
Optimization of sulfur cathode fabrication.
- **University of Washington Seattle**  
Solid state synthesis of sulfur cathode materials.
- **University of Arkansas**  
Material synthesis and sulfur loading.
- **Pacific Northwest National Laboratory (PNNL)**  
Sulfur loaded carbon cloth electrodes
  
- **Department of Chemistry, Wuhan University**  
*In situ* electrochemistry – spectroscopy technique development.
- **Department of Chemistry, Wuhan University of Science and Technology**  
Synthesis of nano particle size sulfur materials
- **Beijing Institute of Technology**  
Sulfur material synthesis
- **Institute of Physics, Chinese Academy of Sciences**  
Electrode structure analysis

# Remaining Challenges and Barriers

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- It remains a challenge of searching for adequate and effective electrolyte additives which can form more stable SEI layer preventing continuous reaction between polysulfide, sulfur and Li anode.
- The lack of adequate additives better than  $\text{LiNO}_3$  to prevent the “shuttle effect”.
- To limit the diffusivity of dissolved sulfur and polysulfide ions beyond the surface coating and encapsulation.
- Sulfur containing electrode with high sulfur loading and decent conductivity.

# Proposed Future Work for *FY 2017* and *FY2018*

## ■ *FY2017 Q3 Milestone:*

Complete the investigation of the chemical equilibriums among dissolved polysulfide ions during the courses of discharge and recharge of Li-S batteries.

## ■ *FY2016 Q4 Milestone:*

Complete the preliminary engineering design and test for the rechargeable Li-S battery including electrode design and cell design.

## *FY2018 work:*

- **Continue investigating the mechanism of sulfur redox reaction by means of in-situ and ex-situ electrochemistry-HPLC/MS/UV techniques. Correlate the distribution of polysulfide ions with the kinds of electrolyte and additives to mitigate “shuttle effect”.**
- **In-situ surface investigation of both sulfur cathode and Li anode during the charge and discharge of Li-S batteries in various electrolytes with different additives. The study will be done by the to-be-optimized in-situ 3D microscope and electrochemical techniques.**
- **Increase the loading of sulfur in engineered carbon structure and explore ways to produce thick sulfur cathode.**
- **Continue explore the new sulfur composite material for performance improvement.**
- **Continuing and enhancing the collaborative research with academic research institutions and industrial partners.**



# Summary

## ■ Relevance

- ✓ *Development of an in-situ 3D microscopic and electrochemical techniques to study the surface of the electrodes.*
- ✓ *With the unique in-situ HPLC-Electrochemical method developed in FY16, to study the complex mechanism of sulfur cathode redox reaction in Li-S batteries (to guide the sulfur cathode material, electrolyte synthesis and cell engineering).*
- ✓ *Continue the investigation of “shuttle effect” by studying the chemical equilibrium of the dissolved elemental sulfur and polysulfide ions, which including the search of the adequate electrolytes for long cycle life Li-S batteries and the additives for stable SEI formation on the Li anode.*

## ■ Approaches

- ✓ *In-situ electrochemical-HPLC/MS/UV.*
- ✓ *Ex-situ X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).*
- ✓ *In-situ electrochemical-3D micro-optical imaging.*

## ■ Technical Accomplishments

- ✓ *The in-situ HPLC/MS-electrochemical technique was optimized. A mechanism was proposed for sulfur redox reaction based on real-time determination of polysulfide ion during the charge and discharge.*
- ✓ *The stability of Li salts with both Li and polysulfide ions was determined. The stability of the SEI layer was also studied.*
- ✓ *An in-situ microscopic-electrochemical cell was designed and built.*

## ■ Proposed Future work

- ✓ *Continue in-situ and ex-situ electrochemistry-HPLC/MS/UV for sulfur redox mechanism study.*
- ✓ *In-situ Keyence 3D microscope and electrochemical techniques for the cathode and anode surface studies.*
- ✓ *Investigating and synthesis porous sulfur cathode for performance improvements.*
- ✓ *Searching for new electrolyte including additives to mitigate shuttle effect.*